

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 1998	3. REPORT TYPE AND DATES COVERED Final, March 1, 1995 - Feb. 28, 1998		
4. TITLE AND SUBTITLE Kinetics of Individual Combustion Reactions Over Wide Temperature Ranges, For Army Models		5. FUNDING NUMBERS DAAH04-95-1-0098		
6. AUTHOR(S) Arthur Fontijn				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Isermann Department of Chemical Engineering Rensselaer Polytechnic Institute 110 Eighth Street Troy, NY 12180-3590		<div style="font-size: 2em; font-weight: bold; transform: rotate(-5deg); position: absolute; right: 0; top: 0;">19981223 123</div>		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER  ARO 33094.2-CH		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  The kinetics of reactions important for models of nitrate ester and nitramine propellant combustion, as well as a reaction of a potential halon replacement fire retardant, has been studied. The experiments, on isolated elementary reactions, have been made in a high-temperature reactor to yield rate coefficients $k(T)$ in realistic temperature ranges. All $k(T)$ given are in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . The $\text{N} + \text{CO}_2 \rightarrow \text{NO} + \text{CO}$ reaction has given an upper limit value of $5 \times 10^{-16}$ at 1140 K and lower values at lower temperatures. This suggests that the reverse reaction is unimportant in dark zones. This is the first investigation of an N-atom reaction at high temperatures by a				
CONTINUED ON REVERSE SIDE				
14. SUBJECT TERMS nitramines, nitrate esters, dark zones, propellant combustion, fire retardants, reaction kinetics		15. NUMBER OF PAGES 9		16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

photolytic technique. As a check on the method, the  $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$  reaction was studied. It yielded  $k(400\text{-}1220 \text{ K}) = 2.0 \times 10^{-18} T^{2.15} \exp(-2557 \text{ K}/T)$ , which in the region of temperature overlap ( $< 910 \text{ K}$ ), is indistinguishable from the literature recommendation. The reaction  $\text{O} + \text{N}_2\text{O}$  has two channels  $\text{NO} + \text{NO}$  and  $\text{O}_2 + \text{N}_2$ . From the measurements, with subsequent modeling,  $k(1370\text{-}3850 \text{ K}) = 1.7 \times 10^{-10} \exp(-14100 \text{ K}/T)$  and  $k(1076\text{-}3340 \text{ K}) = 6.1 \times 10^{-12} \exp(-8000 \text{ K}/T)$ , were obtained for the respective channels. The latter is much larger than reviews suggest and will have a major impact on dark zone models. The ongoing work on  $\text{O} + \text{CF}_3\text{H}$  has yielded the recommendation  $k(630\text{-}1330 \text{ K}) = 3.3 \times 10^{-9} \exp(-10663 \text{ K}/T)$ .

## TABLE OF CONTENTS

	<u>Page</u>
STATEMENT OF THE PROBLEM AND APPROACH	1
RESULTS	1
The N + CO <sub>2</sub> and O <sub>2</sub> Reactions	1
The O + N <sub>2</sub> O Reactions	2
The O + CF <sub>3</sub> H Reaction	4
PUBLICATIONS	5
LIST OF PARTICIPATING SCIENTIFIC PERSONNEL	5
CONTACTS WITH ARMY LABORATORY PERSONNEL	5
REFERENCES	5

## STATEMENT OF THE PROBLEM AND APPROACH

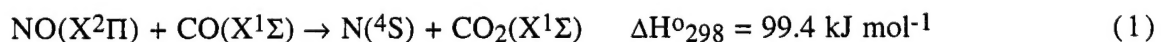
Models of the combustion of nitrate ester and nitramine propellants, especially those for dark zone structures, depend heavily on chemical kinetic input data for individual reactions at the temperatures of interest. Under this grant we have obtained such data for critical reactions. One of our unique HTP (high-temperature photochemistry) reactors has been used to provide these.<sup>1</sup> Such reactors operate in a wall-free pseudo-static mode. This reactor was further used to study a fluorohydrocarbon oxidation reaction, in the context of halon-replacements for Army fire retardants.

All rate coefficients in this report are in  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ . For the  $\Delta H^\circ_{298}$  data, see Ref. 2.

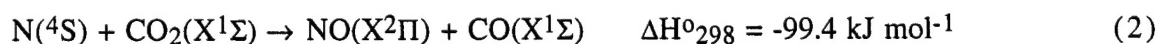
## RESULTS

### The N + CO<sub>2</sub> and O<sub>2</sub> Reactions

One of the critical propellant combustion reactions is



This spin-forbidden reaction is not readily amenable to direct observation, but its reverse



has been studied several times, with conflicting results. Early flow reactor studies in the 295-950 K temperature range suggested a reasonably fast reaction, which was subsequently shown to be merely an N-atom recombination reaction. However, a 2510-3510 K shock tube study<sup>3</sup> of C<sub>2</sub>N<sub>2</sub>/CO<sub>2</sub>/Ar mixtures suggested as a byproduct  $k_2(T) = 1.4 \times 10^{-12} \exp(-1114 \text{ K}/T)$ , which when applied to dark zone temperatures ( $\approx 1200$ – $1500$  K), would suggest reaction (1) as a major radical source.

Our published<sup>4</sup> measurements have spanned the 290-1140 K range and yielded upper limits to  $k_2$  varying from (1 to 50) $\times 10^{-17}$ . This implies that when the corresponding  $k_1$  limit is used in dark zone models that reaction (1) contributes negligibly.<sup>5</sup> Ab initio calculations on  $k_1$  by Chabalowski and Manaa<sup>6</sup> at ARL also

indicate that this reaction can henceforth be removed from dark zone models. This study represents the first time that a reactor of the flash photolysis-resonance fluorescence type has been used for N-atom reactions above 400 K. As a check on the technique we studied a reaction well-known from earlier electrical discharge reactor studies.<sup>7a</sup> i.e.



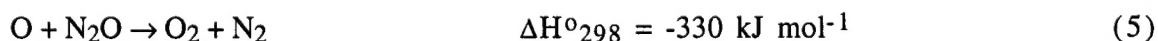
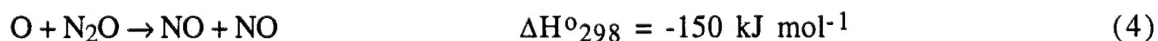
We obtained  $k_3(400\text{-}1220 \text{ K}) = 2.0 \times 10^{-18} (\text{T/K})^{2.15} \exp(-2557 \text{ K/T})$ . This is in excellent agreement with the earlier work and extends the measured temperature range by 300 K.

### The O + N<sub>2</sub>O Reactions

Due to the well-established role of nitrous oxide, N<sub>2</sub>O, as a high concentration intermediate species in the combustion of both nitrate ester and nitramine solid propellants, a clear understanding of the chemistry of this species is critical to combustion models currently being developed for these propellants. The rates of the O + N<sub>2</sub>O reaction are sensitive parameters for detailed propellant dark zone chemistry,<sup>8</sup> which is currently incorporated in interior ballistic design models. The chemistry of N<sub>2</sub>O also pertains to models of NO<sub>x</sub> pollutant formation, which are important both in propellant demilitarization operations and in fossil fuel combustion (i.e., for IC engines and industrial applications).

The study of these title reactions represents a joint effort with Drs. Anderson and Meagher of ARL. Experimental measurements and interpretation was done by us at RPI and modeling studies were made at ARL.

The O + N<sub>2</sub>O reaction has two viable product channels. They are:



Critical reviews, e.g. Ref. 7b, concluded that the two channels have identical rate coefficients:

$$k_4(\text{T}) = k_5(\text{T}) = 1.7 \times 10^{-10} \exp(-14100 \text{ K/T}) \quad (1200\text{-}2000\text{K})$$

However, a recent shock tube study<sup>9</sup> yielded similar results for  $k_4$ , but very different results for  $k_5$ :

$$k_5(T) = 2.3 \times 10^{-12} \exp(-5440 \text{ K}/T) \quad (1940-3340 \text{ K}).$$

Extrapolation of either  $k_5(T)$  or of  $k_t(T) = k_4(T) + k_5(T)$  from Ref. 9 to the lower temperatures typical of propellant combustion yields results several orders of magnitude larger than previously assumed.

The HTP measurements were made using similar methods as used in earlier O-atom studies in that reactor.<sup>1</sup> We obtained

$$k_t(1076-1276 \text{ K}) = 2.7 \times 10^{-9} \exp(-14580 \text{ K}/T) \quad (6)$$

This work represents the first measurements on the overall reaction under conditions in which results are well isolated from effects of other reactions. Thus, there is no dependence of the results on ancillary kinetic data, as in prior studies. The possible influence of  $\text{H}_2\text{O}$  on the reactions, suggested in other studies, was modeled. The modeling predictions indeed indicate the results would be highly sensitive to even a few ppm of  $\text{H}_2\text{O}$  impurities. However, measurements of the apparatus' leak rate show that the possible  $\text{H}_2\text{O}$  impurity concentrations must have been negligibly low. The new measurements concur with Ref. 9 in that the rate coefficients below 1700 K are much larger than previously thought, but they indicate that the value at 1100 K is about 2.5 times lower than extrapolation of the results of Ref. 9 would predict.

The ARL model is based on a state-of-the-art detailed mechanism for the dark zones of solid propellants consisting of ~200 reactions. The appropriate subsets of reactions were extracted from this mechanism and used for the simpler mixtures encountered in the present work. The best rate coefficient information currently available was used without alteration except, of course, rate coefficients for the title reaction were varied. Detailed chemical modeling, mimicking typical conditions described in the various experiments, was done to test assumptions used for determination of  $k_4$  and  $k_5$ . There were three major reasons found for rejection of a given data set from the fitted results: (i) discovery of invalid assumptions, foremost amongst these being important errors concerning the chemical mechanism, (ii) usage of low purity reactants, and (iii) proof that although the mechanism used to model results was essentially correct (matches results well), the results are not very sensitive to the title reaction. The results were fitted to obtain the recommendations for  $k_4$  and  $k_5$ :

$$k_4(1370-3850 \text{ K}) = 1.7 \times 10^{-10} \exp(-14100 \text{ K/T}) \quad (7)$$

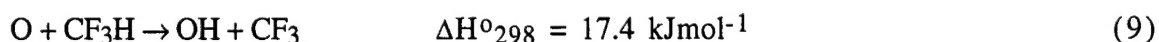
$$k_5(1076-3340 \text{ K}) = 6.1 \times 10^{-12} \exp(-8000 \text{ K/T}) \quad (8)$$

The results for  $k_4$  agree with most prior works. The results for  $k_5$  are much larger in the 1200-1500 K temperature range than the reviews suggest. This difference would have a major impact on propellant models.

One report of this work has been published<sup>10</sup> and another is in preparation.

### The O + CF<sub>3</sub>H Reaction

For environmental reasons chlorine-, and bromine-halons need to be phased out as fire suppressants. Fluorohydrocarbons offer one alternative, but their kinetics needs to be known to evaluate their effectiveness.<sup>11</sup> Originally, we had proposed to study fluoro-olefins but those compounds may no longer be transported. We therefore decided on saturated fluorohydrocarbon reactions and have initiated a study of



The CF<sub>3</sub>H was made available by ARL. Therefore, it is of the same grade as for flames studies used there. O atoms were produced in the same manner as before.<sup>1</sup>

Our measurements have thus far covered the 630 to 1080 K range, for which we obtained  $k_9(T) = 3.7 \times 10^{-9} \exp(-10689 \text{ K/T})$ . They are in good agreement with the laser-flash photolysis shock tube data of Mioyshi et al<sup>12</sup> from 960 to 1330 K.

Combining these results with the present data yields the tentative recommendation:

$$k_9(630-1330 \text{ K}) = 3.3 \times 10^{-9} \exp(-10663 \text{ K/T}) \quad (10)$$

A number of observations over narrower temperature ranges are also available. Such studies tend to have greater uncertainties in their temperature dependence.

Medhurst et al<sup>13</sup> obtained  $k(529-753 \text{ K}) = 2.5 \times 10^{-13} \exp(-3000 \text{ K/T})$  in an apparatus somewhat similar to ours. Their expression gives higher values than ours, which suggests a possible impurities effect. It approaches the present values at the highest temperatures of their work. A flame study, where there are competing reactions, yielded<sup>14</sup>  $k(920-1150 \text{ K}) = 1.8 \times 10^{-12} \exp(-1600 \text{ K/T})$ .

We are continuing these measurements under a complementary AASERT grant. Particularly, we plan to go to higher temperatures and check our results with CF<sub>3</sub>H

obtained from other sources.

## PUBLICATIONS

1. A. Fernandez, A. Goumri, and A. Fontijn, "Kinetics of the Reactions of  $N(^4S)$  Atoms with  $O_2$  and  $CO_2$  over Wide Temperature Ranges", J. Phys. Chem. A 102, 168 (1998).
2. A. Goumri, N.E. Meagher, A. Fontijn, and W.R. Anderson, "Kinetics of the  $O(^3P) + N_2O$  Reaction", 33rd JANNAF Combustion Subcommittee Meeting, CPIA Publication 653, Vol. II p. 403 (1996).

There were no reportable inventions.

## LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

Professor Arthur Fontijn, Principal Investigator

Dr. Abdellatif Goumri, Postdoctoral Fellow

Abel Fernandez, Graduate Student

William F. Flaherty, Group Technician

No degrees resulting from this work have yet been granted. Mr. Fernandez is continuing his work for the PhD.

## CONTACTS WITH ARMY LABORATORY PERSONNEL

Throughout this work we maintained close contact with Dr. W.R. Anderson in ascertaining that our reaction selections would have a direct impact on ARL models for propellant combustion. On the  $O + N_2O$  reactions we collaborated with him and his postdoctoral fellow Dr. N.E. Meagher. Dr. C. Chabalowski provided us with preliminary results of their ab initio study of the  $N + CO_2$  reaction, which corroborates the conclusions from our work. We discussed fire retardation problems with Dr. A. Miziolek, who also helped us to obtain cylinders of  $CF_3H$  and  $C_3F_7H$  needed for studies of their reactions.

## REFERENCES

1. J. Hranisavljevic, G.Y. Adusei, Y. Xun, and A. Fontijn, "High-Temperature Photochemistry (HTP) Studies of the Reactions of Ground State Oxygen Atoms with Chloro-ethylenes", Combust. Sci. & Tech., 101, 229 (1994).



2. Unless otherwise indicate  $\Delta H^\circ_{298}$  values are from M.W. Chase, C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, J. Phys. Chem. Ref. Data 1985, 14, Suppl. 1.
3. D. Lindackers, M. Burmeister, and P. Roth, "High-Temperature Kinetics of the Reaction  $\text{CN} + \text{CO}_2$ ", *Combust. Flame* **81**, 251 (1990).
4. A. Fernandez, A. Goumri, and A. Fontijn, "Kinetics of the Reactions of  $\text{N}(^4\text{S})$  Atoms with  $\text{O}_2$  and  $\text{CO}_2$  over Wide Temperature Ranges", *J. Phys. Chem. A* **102**, 168 (1998).
5. W.R. Anderson, ARL, Private Communication to us, 1997.
6. C. Chabalowski and M.R. Maana, ARL, Private Communication to us, 1997.
7. D.L. Baulch, D.D. Drysdale, D.G. Horne, *Evaluated Kinetic Data for High Temperature Reactions, Vol. 2, Homogeneous Gas Phase Reactions of the  $\text{H}_2/\text{N}_2/\text{O}_2$  System*, Butterworths, London, 1973, a) p. 193, b) pp. 235, 259.
8. W.R. Anderson, N. Ilincic, N.E. Meagher, K. Seshadri, and J.A. Vanderhoff, "Detailed and Reduced Chemical Mechanisms for the Dark Zones of Double Base and Nitramine Propellants in the Intermediate Temperature Regime", 32nd JANNAF Combustion Subcommittee Meeting, *CPIA Publication* 638, Vol. I, p. 197, 1995.
9. D.F. Davidson, M.D. DiRosa, A.Y. Chang, and R.K. Hanson, "Shock Tube Measurements of the Major Product Channels of  $\text{N}_2\text{O} + \text{O}$ ", *Shock Waves*, K. Takayama (Ed.), Springer-Verlag, Berlin, 1992, p. 813.
10. A. Goumri, N.E. Meagher, A. Fontijn, and W.R. Anderson, "Kinetics of the  $\text{O}(^3\text{P}) + \text{N}_2\text{O}$  Reaction", 33rd JANNAF Combustion Subcommittee Meeting, *CPIA Publication* 653, Vol. II, p. 403 (1996).
11. W.L. Grosshandler, R.G. Gann, and W.M. Pitts, Eds., *Evaluation of Alternative In-Flight Fire Suppressants for Full-Scale Testing in Simulated Aircraft Engine Nacelles and Dry Bays*, NIST SP 861, National Institute of Standards and Technology, 1994, pp. 566, 570.
12. A. Miyoshi, K. Ohmori, K. Tsuchiya, and H. Matsui, "Reaction Rates of Atomic Oxygen with Straight Chain Alkanes and Fluoromethanes at High Temperatures", *Chem. Phys. Lett.* **204**, 241 (1993).
13. L.J. Medhurst, J. Fleming, and H.H. Nelson, "Reaction Rate Constants of  $\text{OH} + \text{CHF}_3 \rightarrow \text{Products}$  and  $\text{O}(^3\text{P}) + \text{CHF}_3 \rightarrow \text{OH} + \text{CF}_3$  at 500-750 K", *Chem. Phys. Lett.* **266**, 607 (1997).
14. H. Richter, J. Vandooren, and P.J. VanTiggelen, "Kinetics of the Consumption of  $\text{CF}_3\text{H}$ ,  $\text{CF}_2\text{HCl}$ , and  $\text{CF}_2\text{O}$  in  $\text{H}_2/\text{O}_2$  Flames", *J. Chim. Phys.* **91**, 1748 (1994).